

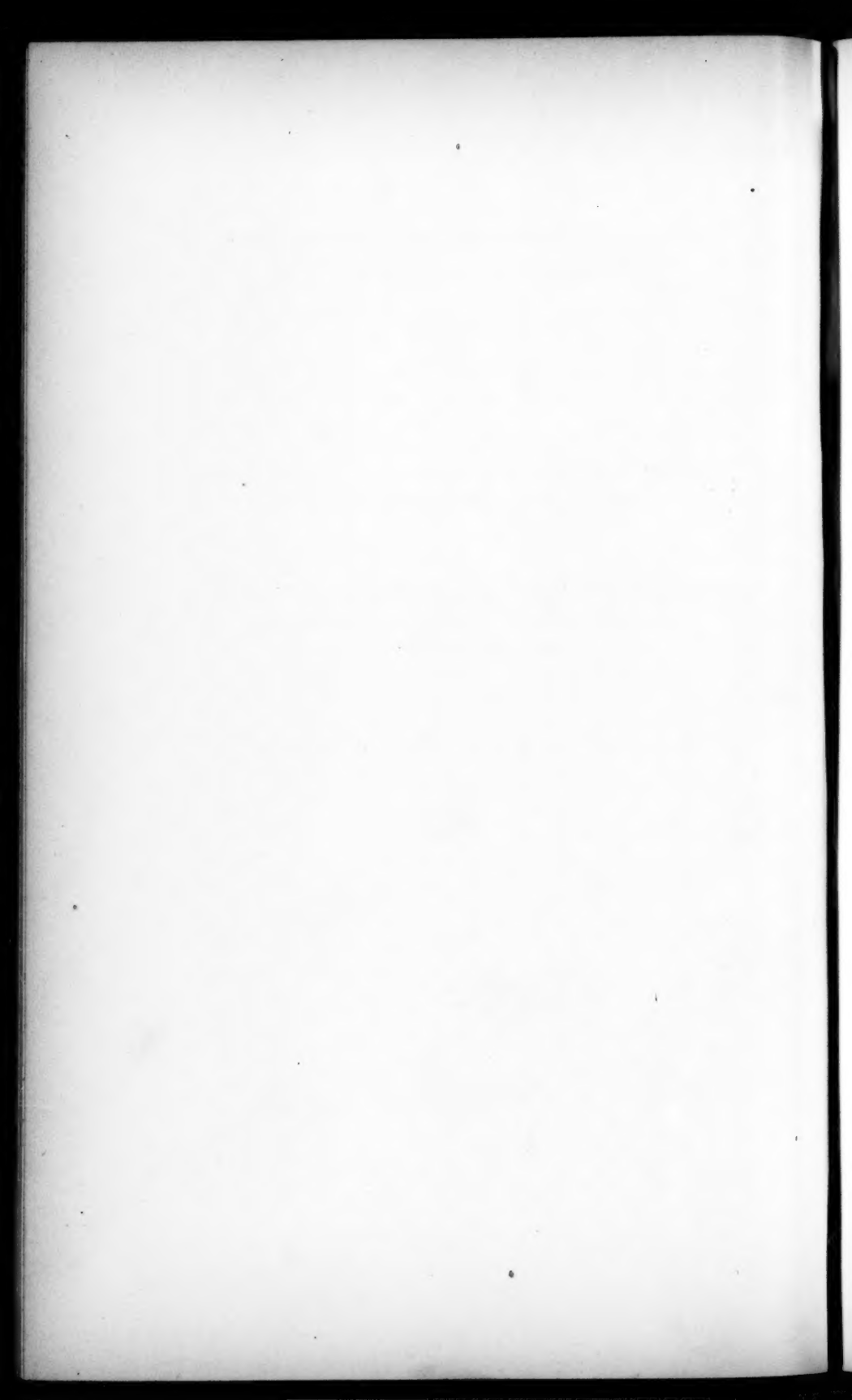
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
CASE SCHOOL OF APPLIED SCIENCE. — XL.

*ON THE SPECIFIC HEAT AND HEAT OF VAPORIZATION
OF THE PARAFFINE AND METHYLENE
HYDROCARBONS.*

BY CHARLES F. MABERY AND ALBERT H. GOLDSTEIN.



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ZATION OF THE PARAFFINE AND METHYLENE
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SINCE 1819, when Dulong and Petit, on the basis of their work on thirteen of the chemical elements, announced the law that atoms of all elementary bodies possess the same capacity for heat, or that the specific heats of the elements vary inversely as their atomic weights, the specific heats of the elements have been important physical constants. With some exceptions, the constant 6.54 represents the product of the atomic weight into the specific heat. Later work showed that this law could be extended to compounds. In 1831, Neumann discovered that compounds, with analogous composition have the same specific heat. Or in a series of compounds with analogous composition the specific heat varies inversely with the molecular weight. These laws apply to approximately forty elements and to solids only at temperatures much below their melting points. The specific heats of many organic compounds have since been determined, and although no law has been stated, it is evident that, in certain homologous series of organic compounds, a condition exists in some of these series analogous to the law of Neumann. For instance, determinations have been made on a few of the alcohols with the following results:

Ethyl alcohol	0.680
Iso-propyl alcohol	0.5286
Iso-butyl alcohol	0.5078
Iso-amyl alcohol	0.4932

That the variations on certain homologous series so far as they have been observed do not conform to a general law, is shown by the following series, in which the specific heats increase with increase in molecular weights:

Methyldichloracetate	0.3202
Ethyldichloracetate	0.3384
Propyldichloracetate	0.3506

In general, the data on specific heats of organic compounds are meagre and not concordant. For the same substance the results of different observers seldom agree in the third decimal place; they often do not agree in the second, and even in the first place (see tables of Landolt and Börnstein). These variations are probably due to the fact that specific heat is materially affected by impurities in the substance, and the temperatures at which it is taken. Then, furthermore, the details of the determinations demand very careful attention to insure concordant results. In the determinations of the hydrocarbons to be described in this paper, it was found that impurities depressed the specific heats very considerably.

Although the paraffine series of hydrocarbons offers the best field for study of an homologous series, very little has been done in the direction of ascertaining the specific heats of these bodies. In a study of distillates separated from Pennsylvania petroleum, by Bartoli and Stracciati,* the specific heats of the following hydrocarbons were determined:

Hexane . . .	C_6H_{14}	.5042	$16^{\circ}-37^{\circ}$
Heptane . . .	C_7H_{16}	.4869	$16^{\circ}-37^{\circ}$
Octane . . .	C_8H_{18}	.5111	$12^{\circ}-19^{\circ}$
Decane . . .	$C_{10}H_{22}$.5057	$14^{\circ}-18^{\circ}$
Tetradecane . .	$C_{14}H_{30}$.4995	
Hexadecane . .	$C_{16}H_{34}$.4963	$15^{\circ}-22^{\circ}$

The inference derived from these results was that the specific heats of these hydrocarbons were remarkably constant.

No data could be found relating to the specific heats of the methylene hydrocarbons C_nH_{2n} , nor those of the series still poorer in hydrogen. With the greatly extended uses of crude petroleum and refined distillates for fuel, in gasoline and oil engines, accurate information concerning specific heat and heat of vaporization is greatly desired.

Having in hand a great variety of hydrocarbons of the various series, which have been prepared in as pure form as possible, and numerous inquiries having been received for more complete information concerning these physical properties, it seemed advisable to make some determinations of these constants.

The hydrocarbons of the series C_nH_{2n+2} , were obtained from Pennsylvania petroleum, those of the other series from California petroleum.

* Gazz. Chim., 1885, 417-445.

Each hydrocarbon had been separated by a long process of distillation, and purified, by treatment with sulphuric acid, sodic hydrate, and drying over sodium.

The determinations were made in a Bunsen ice calorimeter, to which was attached a capillary side tube 70 centimeters long, and the bore of such size that 1 centimeter contained 0.0579 grams of mercury. To maintain the temperature at 0° , the calorimeter was placed in a jar of ice-water with an excess of ice, and this jar was placed in another jar and the space between filled with cotton. The calorimeter was filled with air-free water and dry mercury, and the inside film of ice, 2 to 3 millimeters thick, was formed by evaporation of ether by an air blast within the inner tube. Approximately 2 grams of the hydrocarbon was placed in a small glass stoppered tube of thin glass, whose heat equivalent was determined. The tube and hydrocarbon were heated to 50° , in a larger tube placed in a beaker of water, kept at this temperature for at least 15 minutes, then transferred by a thread to the calorimeter. With care this could be done without loss of heat by radiation. The contraction of the mercury column was from 15 to 25 centimeters.

This method can be used for the paraffine hydrocarbons from C_6H_{14} to $C_{16}H_{34}$, the limit at which the hydrocarbons remain wholly liquid at 0° .

After obtaining the water constant of the apparatus, three to six determinations of each hydrocarbon were made at the temperatures 0° and 50° , with results given in the following table:

	Boiling Points. $^{\circ}$	Specific Heat.
C_6H_{14}	68	.5272
C_7H_{16}	91	.5005
C_7H_{16}	98	.5074
C_8H_{18}	125	.5052
C_9H_{20}	151	.5034
$C_{10}H_{22}$	162	.4951
$C_{10}H_{22}$	172	.5021
$C_{11}H_{24}$	195	.5013
$C_{12}H_{26}$	214	.4997
$C_{13}H_{28}$	226	.4986
$C_{14}H_{30}$	242	.4973
$C_{15}H_{32}$	260	.4966
$C_{16}H_{34}$	275	.4957
Commercial Gasoline		.5135
Crude Ohio Petroleum		.4951

The following table gives the specific heats obtained from the series of methylene hydrocarbons :

	Boiling Points. °	Specific Heat.
C_6H_{12}	68	.5062
C_7H_{14}	98	.4879
C_8H_{16}	119	.4863
C_9H_{18}	135	.4851
$C_{10}H_{20}$	160	.4692
$C_{11}H_{22}$	190	.4819
$C_{12}H_{24}$	212	.4570
$C_{13}H_{26}$	232	.4573
$C_{14}H_{28}$	244	.4531
$C_{15}H_{30}$	263	.4708

It appears from these results that there is a uniform decrease in specific heat with increase in molecular weight. Furthermore the normal hydrocarbons, such as heptane, C_7H_{16} , B. P. 98° , and decane, $C_{10}H_{22}$, B. P. 172° , have higher specific heats than their isomers, such for example as isoheptane, C_7H_{16} , B. P. 91° , and isodecane, $C_{10}H_{22}$ B. P. 162° .

The same variation also appears in the methylene series, with high values for certain members that probably indicate different structural relations.

It is further interesting to observe the materially lower values given by the methylene hydrocarbons as compared with the values for the paraffine hydrocarbons. Whether this be due to greater compactness in the methylene molecule or to some quality of its ring structure, it would be interesting to ascertain.

Perhaps the falling off in specific heat with increasing molecular weight will appear to better advantage when arranged as ordinates on a curve with the molecular weights as abscissae. Only those compounds are given on the curve that are known to be normal, although, of course, this is not known with reference to the higher members. The different values of the isomers heptane and decane is shown on the shorter curve.

This uniform decrease in specific heat with increasing molecular weight in the series C_nH_{2n+2} , suggest a constant relation analogous to the law of Neumann.

If the constant K be expressed in terms of the specific heat multiplied by the molecular weight and the product divided by the number of atoms in the molecule, the specific heats found for the hydrocarbons of this series give the following values for the constant :

Hydrocarbon.	Mol. Wt.	Sp. Heat.	No. Atoms.	K.
C_6H_{14}	86	.5272	20	2.26
C_7H_{16}	100	.5074	23	2.21
C_8H_{18}	114	.5052	26	2.21
C_9H_{20}	128	.5034	29	2.22
$C_{10}H_{22}$	142	.5021	32	2.23
$C_{11}H_{24}$	156	.5013	35	2.23
$C_{12}H_{26}$	170	.4997	38	2.23
$C_{13}H_{28}$	184	.4986	41	2.24
$C_{14}H_{30}$	196	.4973	44	2.23
$C_{15}H_{32}$	210	.4966	47	2.24
$C_{16}H_{34}$	224	.4957	50	2.23

The constant, therefore, for the homologous series of hydrocarbons C_nH_{n+2} is 2.23.

A similar curve drawn for the specific heats of the methylene hydrocarbons, so far as they were determined, show also a regular variation.

The constant K, for the methylene hydrocarbons calculated from the determinations, shows a somewhat higher mean value than that of the paraffine hydrocarbons:

Hydrocarbon.	Mol. Wt.	Sp. Heat.	No. Atoms.	K.
C_6H_{12}	84	.5062	18	2.26
C_7H_{14}	98	.4879	21	2.28
C_8H_{16}	112	.4863	24	2.37
C_9H_{18}	126	.4851	27	2.27
$C_{11}H_{22}$	154	.4819	33	2.25
$C_{15}H_{30}$	210	.4708	45	2.20

The values for the specific heats of both hexane and hexamethylene are higher than should be expected from the results on the other members of the series. These hydrocarbons were well purified, except it seems probable that the distillates contained certain proportions of both.

Determinations were also made of the specific heats of a series of hydrocarbons separated from the high boiling portions of Pennsylvania petroleum. This series is under examination to establish its composition and relations to series, separated from heavy petroleum from other fields. These hydrocarbons were cooled to -10° , and filtered to remove so far as possible the solid hydrocarbons with which they are associated in Pennsylvania petroleum. They have been shown to be members of the series C_nH_{2n} . A more detailed description of these bodies will be presented in a subsequent paper, which is now in preparation.

The following values were obtained for the specific heats of these hydrocarbons:

	B. P.	Sp. Heat.
	°	
$C_{16}H_{32}$	173	.4723
$C_{18}H_{36}$	202	.4723
$C_{20}H_{40}$	223	.4706
$C_{22}H_{46}$	260	.4612
$C_{24}H_{48}$	272	.4586

From data obtained with the paraffine hydrocarbons, there is no opportunity to compare the specific heats, although the sudden drop from the last member examined of the series C_nH_{2n+2} , $C_{16}H_{34}$, specific heat .4957, to the first member of the last series above in which the solid hydrocarbon $C_{16}H_{32}$ had been removed by cooling and filtration, specific heat .4723, shows a marked difference in structure. This relation appears in the longer curve in the table.

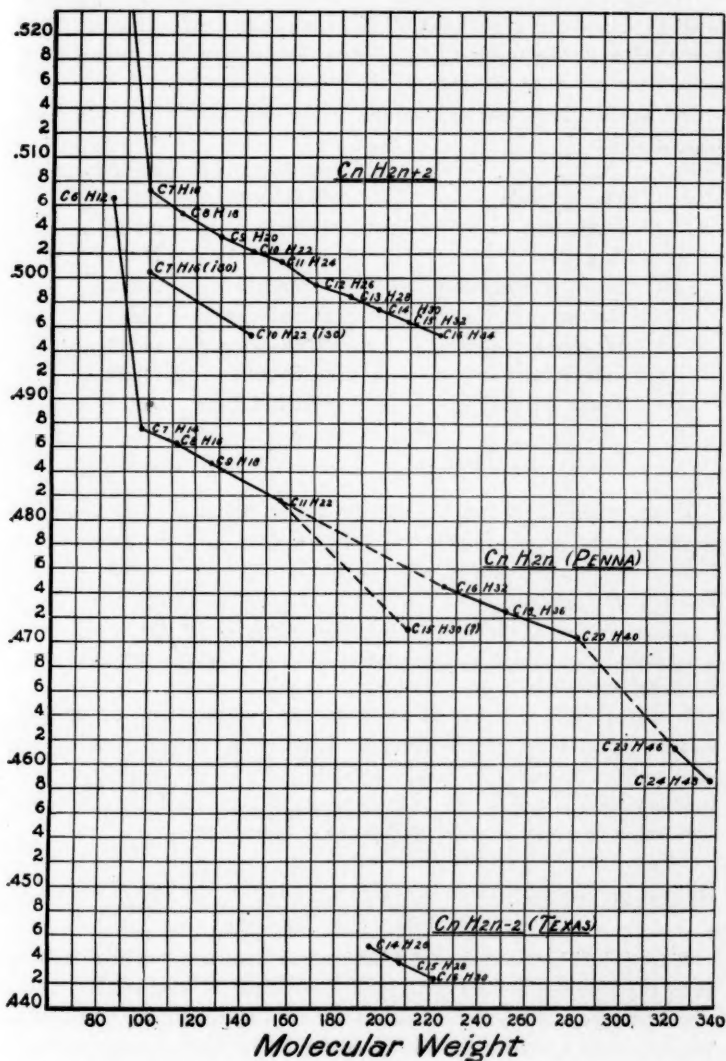
Comparing the last member of the series C_nH_{2n} from California oil $C_{16}H_{30}$, specific heat .4708, with the hydrocarbon $C_{16}H_{32}$, specific heat .4746, it appears that the series C_nH_{2n} from Pennsylvania petroleum is a continuation of the same series from California petroleum. Unfortunately the higher members of the series from California petroleum were not available for comparison. But results already obtained as to the composition, specific gravity, refractive index, &c., are in accord with the specific heats. The specific heat was also determined in several hydrocarbons of the series C_nH_{2n-2} , and the series C_nH_{2n-4} , which had been separated from Texas petroleum with the following results:

SERIES C_nH_{2n-2} .			
	B. P. 50 mm.	Sp. Heat.	K.
	°		
$C_{14}H_{26}$	127	.4447	2.15
$C_{16}H_{28}$	142	.4439	2.15
$C_{18}H_{30}$	162	.4426	2.14

SERIES C_nH_{2n-4} .		
	B. P. 50 mm.	Sp. Heat.
	°	
$C_{21}H_{38}$	218°	.4560
$C_{26}H_{46}$	273°	.4650

The latter results cannot be accepted as reliable, for the quantities of the hydrocarbons were very small, and the oils began to crystallize at 0°. There is no doubt that the specific heats of these hydrocarbons are smaller than those of the preceding series.

To convey a clear idea of the variation in hydrocarbons in the same series, and also to show the differences between the different series, the results are brought together on the following coördinate table :



The regular variation in members of the series C_nH_{2n+2} , appears in its curve, and the differences in what are known to be isomeric forms in the same series. It is further interesting to observe the continuation of the curve representing the members of the series C_nH_{2n} from the curve containing the members of the series C_nH_{2n} from California petroleum. The lower values in the series C_nH_{2n-2} from Texas petroleum form a characteristic curve near the base of the table.

The specific heat was determined in the following crude oils from various fields:

	Specific Gravity.	Specific Heat.
Pennsylvania	0.8095	.5000
Berea Grit	0.7939	.4690
Japanese	0.8622	.4532
Texas (Lucas well)	0.9200	.4315
Russian	0.9079	.4355
Wyoming	0.8816	.4323
California	0.9600	.3980
Texas	0.9466	.4009
Ohio		.4951
Commercial Gasoline		.5135

These values show that the specific heat of the crude oils is an important property from a practical point of view. It also appears that there is no close agreement between specific heat and specific gravity. Pennsylvania oil stands at the head, and Berea Grit with a much larger proportion of volatile constituents is next. Of the heavier oils it appears in general that the specific heats are much lower, but with no definite relation.

It would be interesting to ascertain the specific heats of the less volatile constituents of petroleum from different fields, including the solid hydrocarbons. This would require observations at different temperatures, and it would add to the interest of the data if all determinations could be made within a wide range of temperatures.

HEATS OF VAPORIZATION OF HYDROCARBONS OF THE PARAFFINE AND METHYLENE SERIES.

Since it had been found that a boiling point constant can be calculated from the absolute boiling point, and latent heat of evaporation, which may be used as a basis of a method for the determination of molecular weights, more complete knowledge of the latent heat of evaporation or

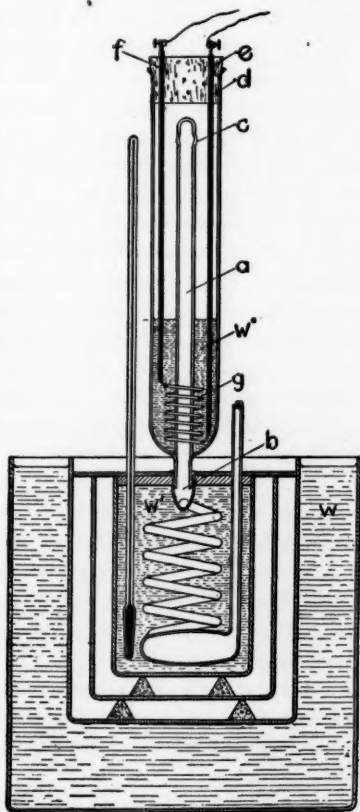
heat of vaporization of liquids at their boiling points has become of great importance. From a practical point of view, the greatly extended use of crude petroleum and its constituents can only be economically continued with the aid of further information concerning the heats of vaporization. Numerous inquiries from persons interested in these directions attest an appreciation of further knowledge on this subject.

In 1885 the following law was proposed by Dudley, on the heats of vaporization of members of a homologous series.*

"In any homologous series the heat of vaporization in a unit of volume of the vapor, under the same conditions of temperature and pressure, is proportional to the density and also to the absolute boiling point." This generalization was based on data selected from determinations of the heats of vaporization of the formiates, acetates, propionates, butyrates, isobutyrate, alcohols, and aromatic hydrocarbons.

With numerous members of the different series of hydrocarbons at hand, it was our intention to determine the latent heat of the series C_nH_{2n+2} , C_nH_{2n} , C_nH_{2n-2} . But the only apparatus available was constructed of glass, which would not withstand the high temperatures necessary in determinations of the hydrocarbons with high boiling points, and the time was too limited to permit of the construction of a metallic apparatus.

For the apparatus used, we are indebted to the kindness of Professor Kahlenberg of the University of Wisconsin, who allowed us to use the



* Journ. Am. Chem. Soc., Vol. XVII., No. 12.

form devised by him, before he had published his description which appeared in the *Journal of Physical Chemistry*, April, 1901.

This apparatus is an ingenious modification of Berthelot's method, in which the substance is heated and volatilized by means of an electric current within the body of the liquid, thus avoiding errors due to external heating. Through the kindness of Professor Kahlenberg and Professor Trevor we are able to show in this connection the form of this apparatus.

In the publication referred to, the apparatus is described as follows: "The retort consists of a tube 17 centimeters long and 5.5 centimeters in diameter, into the bottom of which is fused a tube which fits into a condenser with a ground glass joint. At the other end of the inner tube are two large lateral openings. Glass tubes pass through the cork at the top, and into these are fused the ends of the spiral of platinum wire. This spiral consists of about 40 centimeters of fairly stout platinum wire, to the ends of which are welded short heavy pieces of platinum rod, and these rods are in turn fused into the glass tubes. Long, rather heavy copper wires pass down into the glass tubes, at the bottom of which they are connected with the ends of the platinum rods by means of a few drops of mercury. The calorimeter is covered with a heavy piece of asbestos board and the retort is enclosed in asbestos and cotton batting."

A current from eight to ten amperes, regulated by a rheostat, gave sufficient heat to vaporize from 20 to 30 grams of the oil in from 5 to 6 minutes. The calorimeter, about 2500 cubic centimeters capacity, was made of thin nickel-plated sheet copper. It was elliptical in form, to conform to the shape of the condenser, and was provided with a copper stirrer. The capacity of the calorimeter was reduced, as shown in the figure, by bending closer together the glass tubes leading from the body of the condenser. Temperatures were taken on a Beckman thermometer.

The water equivalent of the calorimeter, condenser, stirrer, and thermometer were found to be 185 grams, practically the same value as the equivalent calculated from the weights and specific heats of the parts of the apparatus.

As mentioned above, this form of the apparatus is limited in this work by the fact that when oils of boiling points higher than 125° are volatilized, the sudden change in temperature at the water line of the condenser is so great that glass will not stand it.

The following results were obtained with a few members of the series C_nH_{2n+2} , as the mean of several observations:

	Boiling Point. °	Heat of Vaporization in Calories.
Hexane, C_6H_{14}	68	79.4
Heptane, C_7H_{16}	98	74.
Octane, C_8H_{18}	125	71.1

Determinations were also made on the methylene hydrocarbons that could be volatilized in this form of apparatus :

	Boiling Point. °	Heat in Calories.
Hexamethylene, C_6H_{12}	68-70	87.3
Dimethylpentamethylene, C_7H_{14}	90-92	81.
Methylhexamethylene, C_7H_{14}	98	75.7
Dimethylhexamethylene, C_8H_{16}	118-119	71.7

These results indicate a rapid falling off in latent heat, with increase in molecular weight. It is to be regretted that we had not the metallic condenser, which would have enabled us to carry these observations up to include the less volatile hydrocarbons of both series. Advantage will be taken of the earliest opportunity to continue this work.

The hydrocarbons used in the work described in this paper were prepared with assistance granted by the Academy from the C. M. Warren Fund for Chemical Research.